International Journal of Engineering Research (ISSN : 2319-6890)
Volume No.2, Issue No. 5, pp : 353-356 01 Sept. 2013

Improvement of Slip Resistance of Rubber Sole by Halogenation

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Abstract: ***Rubber and thermoplastic rubber occupies a considerable extent as bottom sole material in shoes. A surface treatment called "halogenation" is offered on these types of soles to improve adhesion strength between upper and outsole. This is a treatment on Thermo plastic Styrene-butadiene-styrene rubber shoe sole (S1) with a 0.5 % wt. solution of trichloroisocyanuric acid (TCI) in methyl ethyl ketone (MEK) to introduce chlorinated and oxidized moieties on the rubber surface which modifies the surface of the sole for better adhesion with polyurethane adhesive. This mechanism of surface modification is made use of to improve slip resistance property of the soling material. In this study slip resistance in terms of co-efficient of friction (COF) of untreated and treated soles were measured by a slip resistance tester (Model : SATRA STM 603). The results showed that chlorination treatment made on thermo plastic styrene-butadiene-styrene rubber sole with 0.5 % wt TCI produces a noticeable increase in co-efficient of friction values due to increase its surface energy, polarity and surface roughness on the rubber surface.***

Keyword: rubber, surface treatment, co-efficient of friction (COF), slip resistance, surface roughness

1. Introduction

Styrene-butadiene-styrene thermoplastic rubber soles known as TPR soles are commonly used as bottom sole in footwear. Styrene-butadiene-styrene is a block co polymer. In this co polymer, butadiene makes the elastomeric sole soft and elastic while styrene makes the material hard and tough. Among essential properties slip resistance is considered as an important property to avoid frequent accidents caused by slips and falls on slippery surfaces [i, ii].Thermoplastic rubber sole offers a reasonable extent of slip resistance [iii, iv]. Halogination is the process to modify the sole to provide good adhesion between upper and sole[v]. Halogenation of the sole can either increase (or) decrease slip resistance but it seems not to have a significant influence [vi,]. The roles of both footwear and floor surface roughness in the measurement of slipperiness, as well as various techniques, parameters and instruments for roughness measurements are reviewed by Chang et al [vii]. The COF between the shoe sole and floor has been shown to be highly dependent on the roughness of the floor surface [viii- xi]. In this research attempts were made to study the slip resistance of Styrene-butadiene-styrene rubber soles after modifying the surface of the sole using halogenation treatment.

2. Experimental

2.1. Materials

Thermoplastic styrene-butadiene-styrene (S1) rubber sole (Size-42) conventionally used in shoe with the following physical properties (Table 1.) – 10 units were taken for experiment. For floor materials the study used quarry tile with a mean Rz surface roughness of 12.0-14.0 µm. Methyl Ethyl Ketone (MEK), analytical grade, and Trichloroisocyanuric acid (98 wt% purity) were used.

Table 1. Physical properties of styrene-butadiene-styrene rubber shoe sole.

PROPERTY	RESULT
Hardness, Shore A	58 - 63
Density, g/cc	1.01
Tensile strength, MPa	4.5
Elongation at break, %	380
Tear strength, N/mm	11.5
Abrasion resistance Relative volume loss, mm^3	226

2.2 Experiment

The surface of the S1 rubber sole units (for 5 units) was treated with methyl ethyl ketone (MEK) solutions containing 0.5% wt trichloroisocyanuric acid. The sole S1 sample were surface treated with the above solution using a bristle brush applying one uniform coat.

2.3. Experimental techniques

2.3.1. Fourier transform infrared (FTIR) spectroscopy

The chemically surface modified sole units were examined for about 3 µm depth using ATR-IR spectroscopy. ABB-Bomem FTIR spectrometer was used. The angle of incidence of the IR beam was 45^o, and 200 scans were collected and averaged with a resolution of 4 cm^{-1}.

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2.3.2 Scanning electron microscopy (SEM)

The morphological modifications produced on the treated S1 rubber surface were analyzed by SEM. A high resolution scanning electron microscope, FEI Quanta FEG 200 was used. The rubber samples were gold-coated before analysis and the energy of the electron beam was 20 kv.

2.3.3 Contact angle measurements

The wettability of the treated and normal shoe soles were examined for contact angle measurement using a Digidrop GBX goniometer. Surface energy was evaluated from contact angle measurements using the Owends and Wendt approximation [xii].

2.3.4 Surface roughness measurements

Surface roughness of the treated and normal soles was measured using micro-roughness gauge. Surface roughness primarily records surface texture, and a value used for surface analysis (xiii, xiv, xv). In this study, a micro-roughness gauge (Surtronic Duo; Taylor Hobson Ltd., Leicester, UK) with a 5 µm radius diamond stylus was used to measure the center line average (Ra) and maximum height of profile (Rz) among a number of surface roughness parameters. Surface roughness determines the primary texture of the surface, and is normally used for quantification of floor topography. The British Slip Resistance Group reported that measurement of the 'Rz' parameters allow slipperiness to be predicated for range of common materials [xvi].

2.3.5 Measurement of co-efficient of friction

Slip resistance in terms of coefficient of friction (COF) for treated and normal soles were measured using SATRA Model STM 603 slip resistance tester. The testing machine is micro processor controlled friction test equipment, designed to measure the slip resistance of footwear. A test floor surface is located upon the carriage capable of measuring horizontal force beneath the footwear. A desired vertical force is applied on the footwear by applying pneumatic pressure. Both vertical and horizontal forces are measured using load cells. After making contact with the footwear and floor for a shorter period, static delay time, a variable speed motor draws the carriage and floor surface beneath the footwear. Two transducers measure the horizontal force developed between the footwear and floor surface and the ratio of the horizontal and vertical force is displayed as COF on the computer screen. Sole samples under this study were attached on the suitable plastic lasts as per the procedure described in SATRA TM 144:2007 test method [xvii, xviii]. COF studies were made for heel (forward slip), flat (forward slip) and forepart (backward slip). The results were given in Table 4 and comparative results were graphically given in Fig. 3 and Fig. 4.

3. Results and Discussion

The ATR-IR spectrum of the normal untreated S1 rubber (Fig.1) shows typical absorption bands from polybutadiene (C-H stretching at 2923 and 2848 cm^{-1}, -CH_2 scissoring at 1450 cm^{-1}, -CH_2 twisting at 1378 cm^{-1} and out of plane deformation of 1,4-trans C=C at 965 cm^{-1}) and from polystyrene (aromatic C-H stretching at 3024 cm^{-1}, aromatic C-C stretching at 1601 cm^{-1}, out of plane deformation of aromatic C-H at 912 and 697 cm^{-1}) units. There is also C-O-C bending absorption at 871 cm^{-1} of calcium carbonate in the rubber formulation. Surface modified sole units of S1 rubber sole with a 0.5 % wt TCI/MEK solution introduces oxygenated (C=O stretching at 1715 cm^{-1}, C-H bending of –CH_2CO at 1453 cm^{-1} and C-O stretching at 1060 cm^{-1}) and chlorinated (C-H bending –CH_2Cl at 1421 cm^{-1} and C-Cl stretching at 764 cm^{-1}) moieties on the rubber surfaces. Besides, a N-C=O stretching band appears at 1715 cm^{-1}, probably due to the TCI and /or isocyanuric acid crystals, reaction by-product between TCI and rubber, deposited on the treated rubber surface.

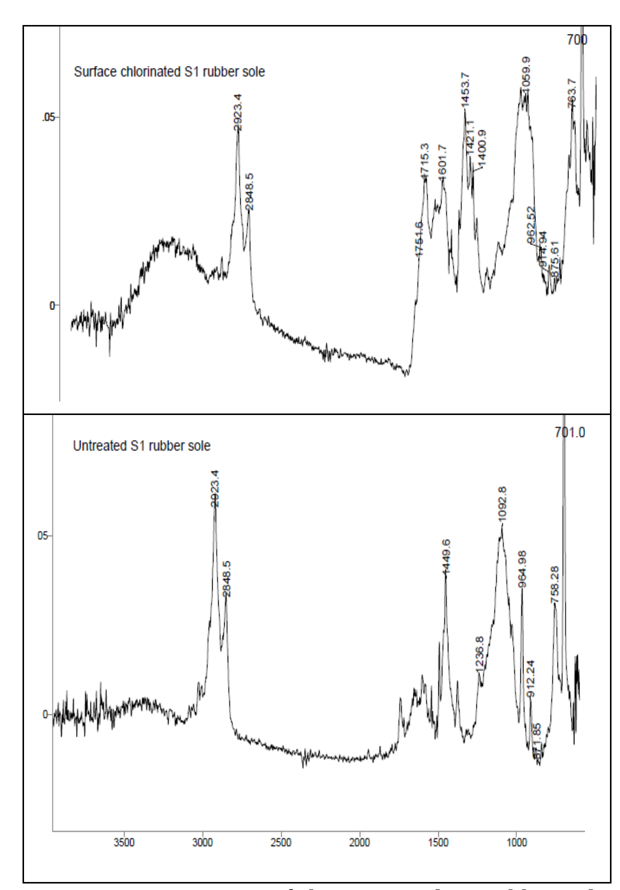


Figure 1. ATR-IR Spectra of the untreated S1 rubber sole and S1 rubber sole surface treated with 0.5 wt% TCI/MEK

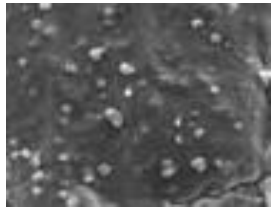



Fig. a Fig. b

Figure 2. SEM micrographs of (a) as untreated S1 rubber sole and (b) S1 rubber sole surface treated with 0.5wt % TCL/MEK

SEM micrograph of normal untreated and treated S1 rubber showed calcium carbonate particles (filler in the S1 rubber formulation) (Fig. 2). On the other hand, some nitrogen is detected on the treated rubber surfaces, probably due to TCI or isocyanuric acid crystals deposited on the treated rubber surface, which has been previously detected in ATR- IR Spectroscopy.

Table 2. Contact angle measurement (bidistilled-deionized water) total (γ_s), polar (γ_s^p) and dispersive (γ_s^d) component of the surface energy of untreated S1 rubber sole and S1 rubber sole treated with 0.5 % wt TCI/MEK

Sample	θ_{H_2O} [°]	γ_s^d [mJ/m²]	γ_s^p [mJ/m²]	γ_s [mJ/m²]
Untreated S1 rubber sole	93	38.0	0.9	40.2
Surface treated S1 rubber sole	75	38.5	5.8	45.2

Table 3. Surface roughness of untreated S1 rubber sole and S1 rubber sole treated with 0.5 % wt TCI/MEK

Sample	Ra µm	Rz µm
Untreated S1 rubber sole	5.25	1.09
Surface treated S1 rubber sole	8.10	17.6

Table 4. COF of untreated S1 rubber sole and S1 rubber treated with 0.5 % wt TCI/MEK

Slip mode	Untreated S1 rubber sole		Surface treated S1 rubber sole	
	Dry	Wet	Dry	Wet
Flat (forward slip)	0.91	0.49	0.96	0.51
Heel (forward slip)	0.83	0.39	0.87	0.43
Forepart (backward slip)	0.82	0.40	0.86	0.42

The introduction of the oxygenated and chlorinated species on the S1 rubber sole surface by the treatment with TCI/MEK produced a decrease of contact angle (evaluated with bidistilled-deionized water) and an increase of the rubber surface energy from 40.2 to 45.2 mJ/m², mainly due to the increase of its polar component from 0.9 mJ/m² to 5.8 mJ/m² (Table 2).

Untreated rubber sole material has shown higher contact angle value due to its non- polar nature. Treatment of S1 rubber sole with 0.5 % wt TCL/MEK solution has shown a noticeable decrease in contact angle values. The decreased contact angle value indicates the increase in the wet ability character of modified rubber and surface energy. The COF values of these modified soles have also improved due to an increased polar nature (Table 4). The SEM analysis of the treated rubber sole surface reveals that the increased wettability of surface is mainly due to the formation of micro cracks (SEM photograph Fig. 2) on the rubber surface.

Figure 3. COF of untreated S1 rubber sole and S1 rubber sole treated with TCI/MEK on dry quarry tile.

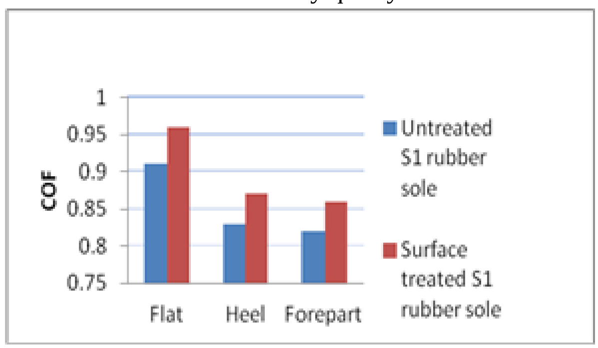
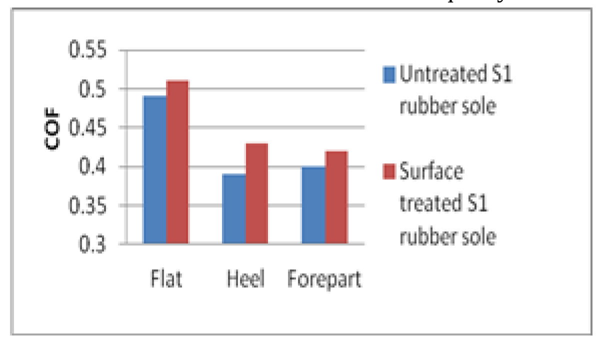


Figure 4. COF of untreated S1 rubber sole and S1 rubber sole treated with 0.5 % wt TCI/MEK on wet quarry tile.



Surface roughness measurement made for normal and treated soles were given in Table 3. It is observed that Ra and Rz values for surface treated rubber material are increased as compared to normal rubber that may be due to the formation of

micro cracks. In dry slip test, higher COF values for flat, heel and forepart slips were observed for treated S1 sole samples than normal S1 sole samples. This trend is observed in wet slip test also (Fig. 3 and Fig. 4).

4. Conclusion

In shoe manufacturing practice thermoplastic rubber soles are treated with halogination chemicals to modify the surface in order to have better adhesion strength between upper and outsole. In this study's it is established that when this surface treatment is extended to the entire surface of the sole with 0.5%TCI/MEK mixture, the polar nature and surface roughness of the soling material are increased due to chemical modification and formation of micro cracks on the material. The contact angle is also decreased, so that surface energy of S1 rubber sole is increased. The above factors influence the coefficient of friction to a reasonable extant and thus increases slip resistance of shoe.

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